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(54) Process for the preparation of fluoride glass and process for the preparation of optical fiber preform using the fluoride glass.

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MATERIALS SCIENCE FORUM, vols. 19-20, 1987, pages 253-258, Trans Tech Publications Ltd, CH; C. JACOBONI et al.: "Vapor deposition of fluoride glasses"

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JAPANESE JOURNAL OF APPLIED PHYSICS, vol. 28, no. 1, January 1989, pages L147–L149; K. FUJIURA et al.: "Organometallic chemical vapor deposition of ZrF4–based fluoride glasses"

R. Belcher et al., J.Inorg. Nucl. Chem. 35 (1973), 1127–43

Description

The present invention relates to a process for the preparation of a highly homogeneous fluoride glass which may be used as a material for optical fibers, laser glasses, glass coatings and lens, and also to a process for the preparation of a fluoride optical fiber and a preform therefor which can provide a long optical fiber having low transmission loss.

Fluoride glasses have therefore been known as optimal materials for optical fibers, glass coatings or films, laser glasses and lens because of their excellent transmission properties within the infrared region range, and expected as glass materials for optical fibers better than silica glasses as having transmission losses of less than 10^{-2} dB/km which is superior over those of the silica glasses.

United States Patent No. 4,718,929 discloses a CVD (chemical vapor deposition) process for preparing metal halides. This prior publication discloses a CVD process for preparing a metal halide glass material which may be used to produce optical fibers used in the infrared region or other optical members, wherein a β-diketone complex containing a fluoride of Be or Al is decomposed in a gaseous phase without using highly corrosive hydrogen fluoride (HF) gas to deposit a BeF_2 (85 to 100 mol%)/AlF_3 (15 to 0 mol%) glass on a substrate. However, strong toxicity and deliquescence of BeF_2 system glasses obstacle practical application thereof. Moreover, the specification of this prior Patent fails to describe the preparation of fluoride glasses containing Ba.

United States Patent No. 4,378,987 discloses a low temperature process for the preparation of an optical fiber in which an organic metal compound is used. In this prior art process, a gaseous halogenation agent, such as BF_3, SiF_4, CoF_2, HF, HCl, $SiCl_4$ or BCl_3, is used for preparing a metal halide by reacting the halogenation agent with a gaseous organic metal compound to produce a glass material made of a solid metal halide. However, the specification of this Patent does not use complexes of Ba and β-diketones.

In conventional processes, fluoride glasses are generally produced through a so-called batch melting process in which solid materials are used. In the batch melting process, solid materials are first weighed, followed by pulverization and mixing, and then the mixed materials are melted in a batch. Thereafter, the melt is rapidly cooled to produce a glass.

However, these processes have the problems that the materials are prone to contamination with transition metals, such as iron, nickel, copper, chromium and cobalt, during the weighing and pulverization steps, and that the materials tend to absorb moisture. Since the impurities including transition elements have aborption peaks within the infrared region, they cause absorption loss within the infrared region of the resultant product. Absorbed water or moisture causes scattering loss. There is also a problem that the wall of the melting appratus is corroded during the step of melting the glass, leading to contamination with impurities. A futher disadvantage is that a large size fluoride glass product cannot be produced since the melt is cast into a mold followed by rapid cooling.

Other processes for the preparation of a preform for optical fibers include a build-in-casting process (reference should be made to Japanese Journal of Applied Physics, Vol 21, No. 1, pp 55 to 56 (1982)), and a modified buit-in-casting process.

However, as has been described above, since a melt is cast into a mold, a large size preform cannot be produced. Furthermore, the known casting processes for production of a core cladding structure include a process wherein a cladding glass melt is flown out before the cladding glass melt has solidified and then a core glass melt is cast (such a process being referred to as build-in-casting process), and a process wherein a core glass melt is cast above the cladding glass melt and the cladding glass melt is flown out from the lower end as the core glass melt is in the semi-solidified state so that the core glass is introduced into the center portion of the cladding glass (modified built-in-casting process). However, these known processes have the disadvantages that a preform for fibers which has a uniform core/clad diameter ratio cannot be produced and that the refraction index profile of the resultant preform for fibers cannot be controlled.

On the other hand, the CVD process has been known as a process for preparing silicaglass optical fibers. It is suited for the synthesis of high purity homogeneous glass. However, when a glass is prepared by the CVD process, compounds of elements constituting the product glass must be heated so that they vaporize. Since fluoride glasses are mainly composed of compounds of alkali metals, alkaline earth metals and rare earth elements which scarcely have sufficiently high vapor pressures at a relatively low temperature, it is difficult to prepare fluoride glasses by the CVD process.

OBJECT AND SUMMARY OF THE PRESENT INVENTION:

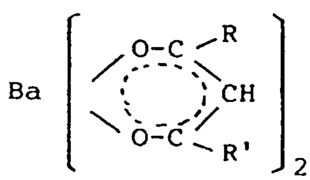
An object of this invention is to provide a process for preparing an optically uniform fluoride glass which may be used as optical fibers, glass coatings, lens or laser glass by a CVD process.

A further object of this invention is to provide a process for preparing a preform for optical fluoride glass fibers which are adapted for use to transmit light between long distant places.

The tasks to be solved by the present invention are to produce a fluoride glass containing barium through the CVD process by the development of a vaporizable material containing barium, to purify the produced glass and to enable production of a large scale glass product. According to a further advantageous feature of the invention, there is provided a process wherein a glass material is deposited internally of a cylinder followed by solidification by collapsing to prepare a preform for a long length and low optical loss fluoride glass.

According to the first aspect of the present invention, there is provided a process for preparing a fluoride glass comprising the step of introducing a gaseous mixture into a reaction system containing a substrate to react with the ingredients of said gaseous mixture in a gaseous phase or on said substrate to deposite a metal fluoride to form a fluoride glass, an improvement characterized in that said gaseous mixture comprising:

a barium - β - diketonate complex serving as a first starting material and represented by the following general formula (1) of:



----------- (1)

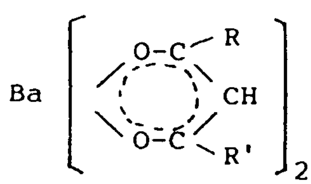
wherein R is an alkyl group having 1 to 7 carbon atoms, R' is a substituted alkyl group having fluorine atoms substituting hydrogen atoms and represented by C_nF_{2n+1} where $\underline{n}$ is an integer of from 1 to 3;

a gaseous or vaporizable compound of the matallic element constituting said fluoride glass, the gaseous or vaporizable compound serving as a second starting material; and

a fluorine - containing gas serving as a fluorinating agent.

According to a second aspect of the present invention, there is provided a process for preparing a fluoride glass comprising the step of introducing a gaseous mixture into a reaction system containing a cylindrical substrate to react the ingredients of said gaseous mixture in a gaseous phase or on the interior wall of said substrate to deposite a layer or fine particles of a fluoride glass, an improvement characterized in that said gaseous mixture comprising:

a barium β - diketonate complex serving as a first starting material and represented by the following general formula (1) of:



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wherein R is an alkyl group having 1 to 7 carbon atoms, R' is a substituted alkyl group having fluorine atoms substituting hydrogen atoms and represented by C_nF_{2n+1} where $\underline{n}$ is an integer of from 1 to 3;

a gaseous or vaporizable compound of the matallic element constituting said fluoride glass, the gaseous or vaporizable compound serving as a second starting material; and

a fluoride - containing gas serving as a fluorinating agent.

The process being further characterized in that said cylindrical substrate containing therein deposited layer or fine particles of a fluoride is heated to solidify by collapsing the same to form a preform for optical fibers.

In the process of the present invention, the first starting material is a barium β-diketonate complex, and the second starting material is a gaseous and/or vaporizable compound of one or more metals, other than barium, which can constitut a fluoride glass. The gaseous and/or vaporizable compounds which may be used as the second starting material include metal halides, organic metal compounds and metal-β-diketonate complexes. Examples of metal halides are halides of metal elements such as the Group Ia, Group IIa, Group IIIa, Group IVa, Group Va, Group Ib, Group IIb, Group IIIb, Group IVb, Group Vb, Group VIb, Group VIIb and Group VIIIb elements. Illustrative examples of the organic metal compounds are trialkyl aluminium and tetraalkoxy titanium. Gaseous or vaporizable metals which constitute complexes with β-diketone include Li and Na of the Group Ia elements, Be, Ca and Sr of the Group IIb elements, Al and In of the Group IIIa elements, Sn and Pb of the Group VIa elements, Sb and Bi of the Group Va elements, Cu of the Group Ib elements, Zn and Cd of the Group IIb elements, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu of the Group IIIb elements, Ti, Zr, Hf and Th of the Group VIb elements, V, Nb and Ta of the Group Vb elements, Cr, Mo and W of the Group VIb elements, and Fe, Co and Ni of the Group VIII elements. These metal elements form complexes with β-diketones and the complexes thus formed have high vopor pressures at relatively low temperatures. Two or more of these complexes of metals with β-diketones may be used in the CVD process for the preparation of a fluoride glass.

The barium-β-diketonate complexes are represented by the general formula of R-CO-CH_2-CO-R' wherein R is an alkyl group having 1 to 7 carbon atoms, R' is a fluorinated alkyl group C_nF_{2n+1} which is produced by substituting hydrogen atoms in alkyl groups by fluorine atoms, and n is an integer of from 1 to 3. Examples of the alkyl group include methyl, ethyl, propyl, butyl, heptyl, phenyl, tertiary butyl and isopropyl groups. Trivial names and abridged notations of beta-diketones which may be used in this invention will be set forth in Table 1.

Table 1

	Ligand Compound; Formula	Trivial Names (Symbol)
1	$(CH_3)_3C-CO-CH_2-CO-C(CH_3)_3$ 2,2,6,6,-tetramethyl 3,5-heptanedione	Dipivaloylmethane (TMH)
2	$CH_3CH_2CH_2-CO-CH_2-CO-C(CH_3)_3$ 2,2-dimethyl 3,5-octanedione	(DMO)
3	$CF_3-CO-CH_2-CO-C(CH_3)_3$ 2,2-dimethyl 6,6,6-trifluoro-3,5-hexanedione	Pivaloyltrifluoromethyl Acetylacetone (PTA)
4	$CF_3-CO-CH_2-CO-CF_3$ 1,1,1,5,5,5-hexafluoro 2,4-pentanedione	Hexafluoroacetylacetone (HFA)
5	$CF_3-CO-CH_2-CO-CH_3$ 5,5,5-trifluoro 2,4-pentanedione	Trifluoroacetylacetone (TFA)
6	$C_2F_5-CO-CH_2-CO-C(CH_3)_3$ 2,2-dimethyl 6,6,7,7-pentafluoro 3,5-heptanedione	(DPH)
7	$C_3F_7-CO-CH_2-CO-C(CH_3)_3$ 2,2-dimethyl 6,6,7,7,8,8,8-heptafluoro 3,5-octanedione	(DHO)

Fluorine-containing gases used in this invention include fluorine gas, and gasesous compounds of fluorine with one or more of hydrogen, halogen elements other than fluorine, carbon, nitrogen, boron, sulfur and silicon. One or more of such gases may be used singly or in combination.

BRIEF DESCRIPTION OF THE DRAWINGS:

Appended drawings include schematic illustrations of processing apparatus which may be used to practise the present invention wherein:

Fig. 1 is a schematic illustration showing an apparatus for preparing a fluoride glass according to one embodiment of the present invention;

Fig. 2 is a schematic illustration showing another apparatus for preparing a fluoride glass according to another embodiment of the present invention;

Fig. 3 is a schematic illustration of an apparatus for preparing a preform for a fluoride optical fiber;

Fig. 4 is a graphic representation showing the results of thermogravimetric analyses of $Zr(HFA)_4$ and $Ba(DHO)_2$;
Fig. 5 is a chart of X-ray diffraction of the $65ZrF_4-35BaF_2$ glass;
Fig. 6 is a chart showing by the real line the infrared absorption spectrum of the $65ZrF_4-35BaF_2$ glass, and also showing by the broken line the infrared absorption sprectrum of a fluoride glass having the same composition and containing ZrF_4 and BaF_2 in the same molar ratio but prepared by the conventional melting process;
Fig. 7 contains upper and lower charts wherein the upper chart shows the scattering distribution of the $65ZrF_4-35BaF_2$ glass, and the lower chart shows the scattering distribution of a fluoride glass having the same composition and containing ZrF_4 and BaF_2 in the same molar ratio but prepared by the conventional melting process;
Fig. 8 is a spectrum chart showing the result of X-ray photoelectron spectroscopy of the $65ZrF_4-35BaF_2$ glass;
Fig. 9 is a chart showing the result of differential thermal analysis of the $65ZrF_4-35BaF_2$ glass;
Fig. 10 is a chart showing the result of differential thermal analysis of a $57ZrF_4-34BaF_2-4.5LaF_3-4.5AlF_3$ glass;
Fig. 11 is a chart showing the result of differential thermal analysis of a $22BaF_2-22CaF_2-16YF_3-40AlF_3$ fluoride glass which has been prepared without using HF gas serving as a fluorinating agent;
Fig. 12 is a schematic illustration showing an apparatus used for collapsing the fluoride glass according to the present invention;
Fig. 13 are charts showing scattering characteristics along the axes of fluoride optical fibers, wherein the upper chart shows the scattering for an optical fiber prepared in accordance with the present invention and the lower chart shows the scattering for an optical fiber prepared by the conventional melting process; and
Fig. 14 is a chart showing the transmission loss sepctrum of a fluoride optical fiber prepared in accordance with the invention.

DETAILED DESCRIPTION OF THE PRESENT INVENTION:

In the process of the present invention, the barium-β-diketonate complex which constitutes the vaporizable first component and/or vaporizable second component containing one or more of metal halides and β-diketonate complexes of metals other than barium may be reacted with a fluorine-containing gas through the CVD technique at a temperature of 0°C to 500°C and at a pressure of atmospheric pressure or subatmospheric pressure.

The substrate contained in a reaction section of the reactor should have a thermal expansion coefficient approximately equal to that of the produced fluoride glass in order that the substrate causes no stress or strain to the resultant fluoride glass during the cooling step, the substrate being preferably made of a glass having excellent anticorrosive properties. The fluoride glass formed is pertinently a so-called fluoride glass or calcium fluoride.

The temperature of the substrate is maintained at a temperature of not higher than the crystallization temperature of the formed fluoride glass, preferably not higher than the glass transition temperature of the formed fluoride glass.

One or more vaporized complexes of β-diketone and metals and fluorine-containing gases, which are introduced into the reaction section of the reactor, are reacted on the surface of the substrate or in the gas phase to form a fluoride glass. The configuration or state of the formed fluoride glass may be a glass film or coating formed when the fluorination reaction takes place on the surface of the substrate, or fine particles formed due to homogeneous nucleation when the fluorination reaction takes place in the gas phase. Irrespective of either state or configuration the fluoride glass has, the vaporised complexes of β-diketone and metals and fluorine-containing gas are adsorbed on the surface of the substrate or the surfaces of fine particles by chemical adsorption, where they react with accompanying thermal decomposition to form metal fluorides. When the temperature of the substrate or the temperature of the gas phase is maintained at a temperature of not higher than the glass transition temperature of the formed fluoride glass, the mobility of fluoride molecules on the growing surface is maintained at a low level so that the random adsorption state of the metal-β-diketonate complexes is frozen even after the fluorination, for example, by HF gas. As a result, the amorphous state can be frozen without any special measure similarly as in the case of being rapidly cooled by quenching. Thus, a highly homogenous fluoride glass conatining no separate crystallite can be produced. Hence, a fluoride glass having a composition which could not be prepared by conventional processes because of their poor glass-forming abilities can be prepared by the present

invention.

In the process for pr paring a fluoride glass, according to the present invention, fluoride glass coatings are serially deposited on the substrate, or alternatively fine particles of fluoride glass are initially formed and then solidifi d. Accordingly, by varying the reaction time, the thickness of the resultant fluoride glass coating may be easily controlled. Also, a large size fluoride glass block may be produced by continuing reaction for a long time.

A further advantage of the process for preparing a fluoride glass, according to the present invention, resides in exclusion of contamination by impurites from external sources. This is due to the fact that the starting organic metal compound, i.e. a metal-β-diketonate complex, is processed continuously from the vaporization thereof to the formation of a fluoride glass without exposure to air. A still further advantage of the process of the present invention resides in exclusion of contamination caused by corrosion of the wall of a crucible or container used at the melting step, since no crucible or like container is needed in the process of the present invention. Upon vaporization of the starting material, impurities, such as transition elements or metals, may be separated. Accordingly, a high purity fluoride galss containing exteremely little impurity, which might cause optical absorption or scattering, can be prepared by this invention.

The preform for a fluoride optical fiber, according to the present invention, may be produced initially by depositing a fluoride glass over the inner peripheral wall of a cylindrical substrate and then heating the cylinder to collapse the deposited glass. In accordance with the process of the present invention, by heating the glass coating or fine glass particles deposited over the inner wall of the cylinder to a temperature of not higher than the crystallization temperature of the formed glass while maintaining the pressure in the cylinder at a subatmospheric pressure, a preform may be produced by collapsing the formed glass without causing crystallization thereof. Prior to collapsing, oxygen-containing impurities, such as OH groups, adsorbed on the surface of the coating or fine particles of glass are removed by heating the glass to a temperature of not higher than the glass transition temperature while purging the interior of the cylinder with a halogen-containing gas, such as F_2, Cl_2, NF_3, CF_4, SF_6, HF or HCl. These oxygen-containing impurities form oxides which cause scattering if they remain in the product, and thus should be removed. According to a further aspect of the present invention, one and of the produced preform may be drawn during the heating and collapsing step so that collapsing and drawing may be effected simultaneously.

Since oxygen-containing impurities are removed by the use of a halogen-containing gas and a preform or an optical fiber can be produced without exposure to the external environment, according to the process of the present invention, the resultant fluoride glass optical fiber is free from optical absorption or scattering due to the presence of impurities and has low transmission loss. Moreover, by varying the time during which the glass product is deposited, the core/cladding diameter ratio of the optical fiber can be easily controlled. The refractive index profile of the optical fiber can also be easily controlled by changing the feed rate of the starting material continuously. The cylindrical substrate on which the fluoride glass is deposited may be selected from any materials as long as they have viscosities approximately equal to that of the product at the temperature at which collapsing or drawing is effected in addition to the condition that the interior wall of the cylindrical substrate withstands the corrosive reaction of the fluorine-containing gas. An example of such a cylindrical substrate is a cylindrical tube made of a glass, metal or a polymer or a tube having a multi-layered structure made of one or more of glasses, metals and/or polymers. A large size preform may be produced by selecting a material from which a large size substrate tube is prepared, so that a long fluoride glass optical fiber may be produced therefrom.

The process for preparing a fluoride glass, according to the present invention, allows chemical vapor deposition of a fluoride glass which could not be practised by the conventional technology. The process of the present invention produces a homogenous fluoride glass which contains a lesser amount of impurities as compared with those produced by the conventional melting processes. Alkali metals, alkaline earth metals and rare earth elements, the compounds thereof having high vapor pressures at low temperatures being not known by now, form complexes with β-diketonates and the thus formed complexes have high vapor pressures at low temperatures, so that the CVD process can be applied by using them to prepare fluoride glasses having the compositions which could not be produced by the conventional processes. Since the metal-β-diketonate complexes have high vapor pressures at low temperatures, the processing temperature during the glass preparation step can be maintained at a low temperature. Thus, even a thermally unstable glass composition can be prepared at a temperature lower than the crystallization temperature thereof. Further, it is made possible to prepare a fluoride glass optical fiber having a controlled core/cladding diameter ratio and having a controlled refractive index distribution, which could not be prepared by the conventional casting process.

An exemplary apparatus for preparing a fluoride glass, according to the present invention, is shown in Fig. 1. Referring to Fig. 1, the interior of a reaction chamber 1 is controlled to have an adjusted reduced

pressure by means of an evacuation system including a rotary pump (R.P.), and has a fluorine-containing gas inlet 1a and a vaporizable material inlet 1b. The reaction chamber 1 is heated by a heater 2 surrounding the reaction chamber 1. At the substantial center of the reaction chamber 1, a substrate 3 is placed on a heater 4 to receive thereon a depositing fluoride glass. Two evaporators 6a, 6b contain two different vaporizable materials 5a, 5b, and are connected to the vaporizable material inlet 1b of the reaction chamber 1 through vaporizable material feed pipes 7a, 7b which meet with each other upstream of the inlet 1b. Not-shown carrier gas introduction means are provided at the side opposite to the feed pipes 7a, 7b connected to the evaporators 6a, 6b so that a carrier gas, such as argon, is introduced into the reaction chamber 1. Each of the evaporators 6a, 6b is heated respectively by heaters 8a, 8b to a suitable temperature. Outer peripheries of the feed pipes 7a, 7b are heated by heaters 9a, 9b. A fluorine-containing gas, such as hydrogen fluoride gas HF is suppied from the fluorine-containing gas inlet 1a through a fluorine-containing gas supply pipe 11 which is kept warm by a heater 9c.

The reaction chamber 1, the evaporators 6a, 6b and vaporizable gas feed pipes 7a, 7b may be made of aluminium, nickel, copper, iron or a nickel alloy of Ni-Cu system. It is preferrred that aluminium is used for the material of these parts, since it has excellent thermal conductivity to prevent condensation of the vaporizable materials and is also resistant to corrosion by fluorine-containing gases. When aluminium is used to construct the reaction chamber 1, the evaporators 6a, 6b and voporizable gas feed pipes 7a, 7b, the temperature in the apparatus is uniformalized to prevent condensation of the starting materials. As the result, a fluoride glass having a stable composition is prepared, and hydrogen fluoride (HF) gas and fluorine (F_2) gas which are effective fluorination agents for the fluorination of metal-β-diketonate complexes may be used in the apparatus. Of course, contamination by impurities due to corrosion of the interior wall of the apparatus is avoided.

As the heat source for the heater 4, ultraviolet rays, infrared rays, far infrared rays, radio frequency induction plasma and microwave induction plasma may be used.

By the provision of a window made of, for example, CaF_2 over the substrate 3, the fluoride glass may be prepared while inspecting the depositing glass through a silica fiber scope.

Another embodiment of the apparatus for preparaing a fluoride glass is shown in Fig. 2, wherein aluminium reaction chamber 1 is maintained at a pressure of 1333.2 Pa (10 mmHg) by means of a rotary pump (RP). Within the reaction chamber 1 a substrate 3 is placed which is a plate of CaF_2. Only the substrate 3 is heated by a heater 2. The reaction chamber 1 has first and second inlet ports 1a, 1b respectively. A gas stream containing an organic metal compound and a metal halide is introduced through first inlet port 1a and a stream of a fluorine-containing gas is introduced through second inlet port 1b. In a sublimation chamber, zirconium particles 5 are reacted with a bromine gas to form $ZrBr_4$. The reaction chamber 1 is supplied with $ZrBr_4$ while using argon as a carrier gas through a first feed pipe 7 which is connected through a variable leak valve to the first inlet port 1a.

On the other hand, a metal-β-diketonate complex of an organic metal compound is vaporized and fed to the reaction chamber 1 while using argon as a carrier gas. The first inlet port 1a is connected to a second feed pipe 11 through a viariable leak valve. The second feed pipe 11 is connected to an evaporator 14 which is surrounded by a feed furnace 12, a metal-beta-diketonate complex 13 being contained in the evaporator 14. Argon is introduced into the mass of metal-β-diketonate complex 13 while heating the evaporator 14 so that the vaporized metal-β-diketonate complex is fed to the reaction chamber 1 via the second feed pipe 11.

As the fluorine-containing gas, hydrogen fluoride gas HF is fed through a third feed pipe 11 and second inlet port 1b to the reaction chamber 1. A variable leak valve adjusts the feed rate of HF. A fluoride glass is deposited on the substrate 3 in the reaction chamber 1 by the thermal decomposition of the metal-β-diketonate complex and the fluorination by the metal halide and hydrogen fluoride gas.

Fig. 3 shows an appratus for preparing a preform for fluoride glass optical fibers. In fig. 3, a reaction chamber 1 is evacuated by an evacuation system having a rotary pump (R.P.) so that the pressure in the reaction chamber 1 is adjustably reduced to subatmospheric pressure. The reaction chamber 1 is made of aluminium and has a first inlet port 1a through which a voporizable starting mateial is introduced and a second inlet port 1b through which a fluorine-containing gas is introduced. The reaction chamber 1 is maintained at 250°C, in its entirety, by a heater 2, and the pressure in the chamber 1 is maintained at a pressure of 1333.2 Pa (10 mmHg).

Into the reaction chamber 1, a cylindrical tube 3 is disposed and made of a fluoride glass having a composition in molar ratio of $39.7ZrF_4-13.3HfF_4-18.0BaF_2-4.0LaF_3-3.0AlF_3-22NaF$. Through the first and second inlet ports 1a, 1b of the reaction chamber 1 introduced are a gas stream of a metal-β-diketonate complex and a fluorine-containing gas, respectively.

EXAMPLES OF THE PRESENT INVENTION:

In order that the present invention should be more fully understood, presently pr ferred Examples of the invention will be set forth below.

Example 1

In the apparatus shown in Fig. 1, a complex $Zr(HFA)_4$ which is a complex of hexafluoroacetylacetone (hereinafter referrred to as HFA) and zirconium was used together with a complex $Ba(DHO)_2$ which was a complex of 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (hereinafter referred to as DHO)and barium. Hydrogen fluoride gas (HF) was used as the fluorine-containing gas. The interior of the reaction chamber 1 was maintained at a pressure of 1333.2 Pa (10 mmHg), and at a temperature of 205°C by using the heater 2. The substrate 3 was a CaF_2 plate which was heated to 250°C by the heater 4.

The results of thermogravimetric analyses of $Zr(HFA)_4$ and $Ba(DHO)_2$ used as the vaporizable materials are shown in Fig. 4. Weight decrease due to vaporaization was observed at about 60°C for $Zr(HFA)_4$ and at about 200°C for $Ba(DHO)_2$. $Zr(HFA)_4$ was maintained at 60°C in the evaporator 6a by means of the heater 8a and $Ba(DHO)_2$ was maintained at 200°C in the evaporator 6b by means of the heater 8b. The voporized gases were introduced into the reaction chamber 1 while being carried by argon supplied from a carrier gas supply means (not-shown). The feed rate of HF was controlled by a mass flow controller. The feed pipes 7a, 7b and 11 were maintained, respectively, at 65°C, 205°C and 30°C by the heaters 9a, 9b and 9c.

$Zr(HFA)_4$ and $Ba(DHO)_2$ introduced in the reaction chamber 1 were converted into fluorides in the gaseous phase by the following reactions, and deposited on the substrate 3 to form a fluoride glass.

$$Zr(HFA)_4(g) + 4HF(g) \rightarrow ZrF(g) + 4HFA(g)$$
$$Ba(DHO)_2(g) + 2HF(g) \rightarrow BaF_2(g) + 2DHO(g)$$
$$xZr(DHO)_2(g) + yBaF_2(g) \rightarrow xZrF_4 + yBaF_2(s)$$

In the reaction equations set forth above, (g) indicates the gaseous state and (s) indicates the solid phase.

ZrF_4 and BaF_2 formed by the above reactions and deposited on the substrate 3 had low mobilities on the substrate since the temperature of the substrate was maintained at a temperature lower than the transition temperatures of the fluoride glasses, and thus frozen in situ without changing positions. As a result, the non-equilibrium state was realized similarly as in the case of quenching. The fluoride glasses were serially deposited to prepare a glass coating or a glass bulk.

The fluorination reactions of $Zr(HFA)_4$ and $Ba(DHO)_2$ took place independently. The rates of preparation of ZrF_4 and BaF_4 by the reaction between $Zr(HFA)_4$ and HF and between $Ba(DHO)_2$ and HF were kept unchanged in the reaction of $Zr(HFA)_4-Ba(DHO)_2-HF$. Accordingly, the Zr/Ba ratio in the formed glass could be easily controlled by adjusting the flow rate of argon used as the carrier gas.

In this Example, $Zr(HFA)_4$ was supplied at a feed rate of 100 cc/min, $Ba(DHO)_2$ was supplied at a feed rate of 50 cc/min and HF was supplied at a feed rate of 150 cc/min and reaction was continued for 2 hours, whereby a glass block having a composition of $65ZrF_4-35BaF_2$ was obtained.

The X-ray diffraction chart of the thus prepared glass is shown in Fig. 5, and the infrared absorption spectrum chart is shown in Fig. 6. In Fig. 6, the infrared absorption spectrum of a fluoride glass having the same composition and prepared by a conventional melting process is shown by the broken line. The distribution of scattered light intensity relative to the substrate of $65ZrF_4-35BaF_2$ glass upon launching of a He-Ne laser was measured. For comparison, a similar scattering distribution of a fluoride glass prepared through the conventional process was determined. The lower chart of Fig. 7 shows the scattering distribution of the $65ZrF_4-35BaF_4$ prepared by the process of the present invention, and the upper chart in Fig. 7 shows the scattering distribution of a glass having the same composition and prepared by the conventional process.

In the X-ray diffraction chart, the fluoride glass prepared by this Example does not show a diffraction peak due to the presence of crystal. In the infrared absorption spectrum, the fluoride glass prepared by this Example does not show an absorption peak at about 2.9 μm due to the presence of OH group, whereas the fluoride glass prepared by the conventional process does show an absorption due to the presence of OH group. It is appreciated from the result of infrared absorption spectrum that the fluoride glass prepared by the process of this invention is a fluoride glass in which the concentration of hydroxyl group is extremely low. In should be appreciated, from the results shown in Fig. 6 that compared to the fluoride glass prepared by the conventional process, the scattering caused by oxides is significantly decreased in the glass

produced by the present invention. In the fluoride glass prepared by the conventional process, a portion of hydroxyl groups present on the surfaces of the starting materials form oxides during the melting step which cause scattering in the formed glass. On the contrary, the fluoride glass of the present invention is prepared through continuous steps including the step of vaporizing the starting materials and the step of formation of the glass, leading to reduction of oxide impurities as shown in Fig. 7.

Fig. 8 is a spectrum chart showing the result of X-ray photoelectron spectroscopy of $65ZrF_4-35BaF_2$ glass. The fluoride glass prepared by the process of the present invention is composed only of zirconium, barium and fluorine, hence signals showing the presence of C_{1S} and O_{1S} are not detected, showing that no organic materials are present. It should be appreciated from the result that the reaction between a metal-β-diketonate complex and a fluorine-containing gas can proceed at a low temperature to prevent impurities in the resultant glass. Since the metal-β-diketonate complex in the process of this invention can be vaporized at a low temperature so that the temperature throughout the overall preparation step can be maintained at a relatively low temperature, a homogenous glass can be prepared at a temperature lower than the crystallization temperature of the formed fluoride glass, even for the preparation of fluoride glasses which have low glass transition temperatures and are thermally unstable.

By using β-diketonate complexes of other metal elements, fluoride glasses containing different metallic constituents may be prepared. The compositions of formed fluoride glasses may be easily controlled by adjusting the flow rate of argon used as the carrier gas. The result of differential thermal analysis of $65ZrF_4-35BaF_2$ glass is shown in Fig. 9. The glass transition temperature of the glass was 270 °C and the crystallization temperature was 330 °C.

Example 2

The same apparatus was used as in Example 1 and as shown in Fig. 1. Additionaly, two evaporators similar to the evaporators 6a, 6b were provided and connected to the feed pipe 7b. Similarly as in Example 1, a fluoride glass was prepared. $La(DHO)_3$ was contained and maintained at 180 °C in one of the additional evaporators, and $Al(DHO)_3$ was contained and maintained at 90 °C in the other of the additional evaporators.

A 5.5 mm thick glass was deposited on a CaF_2 substrate for a reaction time of 2 hours. The formed fluoride glass had a composition, in mol%, $57ZrF_4-34BaF_2-4.5LaF_3-4.5AlF_3$.

The formed fluoride glass had an improved thermal stability, compared with the glass produced in Example 1, by the addition of LaF_3 and AlF_3, and no change in density of scatters was observed even after subjected to a heating treatment for an hour.

The result of differential thermal analysis of the $57ZrF_4-34BaF_2-4.5LaF_3-4.5AlF_3$ glass prepared by Example 2 is shown in Fig. 10. The glass transition temperature of the glass was 301 °C, and the crystallization temperature thereof was 395 °C.

Example 3

A fluoride glass was prepared as in Example 2 except that triethylaluminium $Al(C_2H_5)_3$ was contained in the evaporator in place of $Al(DHO)_3$ while using a similar apparatus to that used in Example 2. The evaporator containing $Al(C_2H_5)_3$ was maintained at 40 °C.

A glass having a thickness of about 5.5 mm was deposited on the CaF substrate for a reaction time of 2 hours. The formed fluoride glass had the same composition as that of the glass prepared by Example 2, the composition of the formed glass being represented by $57ZrF_4-34BaF_2-4.5LaF_3-4.5AlF_3$. The result of X-ray photoelectron spectroscopy revealed that no carbon was remained in the resultant glass. The results of infrared spectroscopy, X-ray diffraction, scattering distribution analysis and differential thermal analysis were equivalent to those of the glass prepared by Example 2, and it was revealed that an optically homogenous glass could be prepared by using organic metal compounds in lieu of β-diketonate complexes. Likewise, glasses could be prepared by using 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (DHO) complexes of other rare earth metal elements, such as Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, in place of La. The results of differential thermal analyses showed that the glasses had equivalent thermal stabilities. Particularly, a glass having no absorption peak within the medium infrared region was obtained by using a complex of Gd.

Example 4

While using the same apparatus as used in Example 1 and shown in Fig. 1, three additional evaporators were provided and a fluoride glass was prepared through a similar procedure as described in Example 2.

The additional evaporators contained $La(DHO)_3$, $Al(DHO)_3$ and Na(TMH) and were matintained, respectively, at 180 °C, 60 °C and 150 °C.

A glass having a thickness of about 6.5 mm was deposited on the CaF_2 substrate within a reaction time of 2 hours. The formed glass had a composition represented by $51ZrF_4-20BaF_2-4.5LaF_3-4.5AlF_3-20NaF$ (in mol%).

By the addition of NaF to the fluoride glass of Example 2, the thermal stability of the fluoride glass was improved. The density of scatters was not changed even after the thermal treatment effected at 300 °C for 5 hours. The result of differential thermal analysis showed that the glass prepared by this Example had a glass transition temperature of 260 °C and a crystallization temperature of 373 °C. A similar glass was prepared by using Li(TMH) in place of Na(TMH), and the formed glass containing 20 mol% of LiF was subjected to differential thermal analyssis to reaveal that it had a glass transition temperature of 252 °C and a crystallization temperature of 348 °C.

Also the $La(DHO)_3$ was mixed, respectively, with 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (DHO) complexes of In, Sn, Pb, Sb, Bi, Zn, Cd, Ti. Th, Nb, Ta, Mo and Mn to prepare glasses containing 1 to 10 mol% of each of fluorides of these metals. The fluoride glasses showed a crystallization temperature shift by 2 to 15 °C to the lower temperature side, as compared to the glass of this Example. Each of these glasses had a thickness of about 5 mm and no scattering was observed.

Example 5

A fluoride glass was prepared similarly as in Example 2 except that $Hf(HFA)_4$ was charged in the evaporator in place of $Zr(HFA)_4$. The evaporators charged with $Hf(HFA)_4$, $Ba(DHO)_2$, $La(DHO)_3$ and $Al(DHO)_3$ were maintained, respectively, at 55 °c, 200 °C, 180 °C and 90 °C. The feed rates were 100cc/min for $Hf(HFA)_4$, 150 cc/min for $Ba(DHO)_2$, 13 cc/min for $La(DHO)_3$, 13 cc/min for $2Al(DHO)_3$ and 200 cc/min for HF.

The reaction was continued for 2 hours, whereby a fluoride glass having a thickness of about 5 mm was deposited on the CaF_2 substrate. The result of elementary anlaysis through the X-ray photoelectron analysis revealed that the formed glass had a composition in molar ratio of $57HfF_4-34BaF_4-4.5LaF_3-4.5AlF_3$. The refractive index of the thus formed glass was $n_D = 1.50$.

The result of differential thermal analysis revealed that the transition temperature of the glass was 315 °C and the crystallization temperature was 403 °C. Thus, an HfF_4 system fluoride glass having a thermal stability substantially equivalent to that of the ZrF_4 system glass was prepared.

Example 6

A fluoride glass was prepared similarly as in Example 2, except that $Ba(DHO)_2$, $Ca(DHO)_2$, $Y(DHO)_3$ and $Al(DHO)_3$ were used as the starting materials and hydrogen fluoride (HF) gas was not used as the fluorine-containing gas.

The evaporators charged with $Ba(DHO)_2$, $Ca(DHO)_2$, $Y(DHO)_3$ and $Al(DHO)_3$ were maintained, respectively, at 200 °C, 180 °C, 140 °C and 95 °C. The feed rates of the metal-β-diketonate complexes were kept at 55 cc/min for $Ba(DHO)_2$, 55 cc/min for $Ca(DHO)_2$, 40 cc/min for $Y(DHO)_3$ and 100 cc/min for $Al(DHO)_3$. The temperature of the substrate was maintained at 380 °C. The reaction was continued for 2 hours to obtain an about 8 mm thick fluoride glass depostited on the CaF_2 glass. The formed fluoride glass was analysed by X-ray photoelectron analysis to find that it had a composition of $22BaF_2-22CaF_2-16YF_3-40AlF_3$ (molar ratio). No residual carbon was observed. It was thus found that the ligands of β-diketonate complexes used as the starting materials were decomposed in the gaseous phase to act as the fluorinating agents, since DHO (2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione) contains fluorine atoms. The result of differential thermal analysis of the formed fluoride glass is shown in Fig. 11. The result shows that the glass transition temperature of the formed fluoride glass is 430 °C, and the crystallization temperature thereof is 560 °C. While the crystallization temperature of a fluoride glass having the same composition and prepared through the conventional melting process is 535 °C, and thus the crystallization temperature of the fluoride glass obtained by the process of the present invention is higher than that of the glass prepared by the conventional process by 25 °C. This shows that the thermal stability of the fluoride glass prepared by the present invention is improved over that of the fluoride glass prepared by the conventional melting process. The improvement in thermal stability is attributed to the removal of oxide impurities in the fluoride glass prepared according to the present invention, the oxide impurities being not removed in the fluoride glass prepared by the conventional melting process. The refractive index of the fluoride glass prepared in this Example was $n_D = 1.44$. Fluoride glasses were prepared by using $Sr(DHO)_2$

and $Ca(DHO)_2$ in place of $Mg(DHO)_2$ and using MgF_2 and SrF_2 as the substrate in place of CaF_2. About 7 mm thick glasses free of scatters were prepared.

Example 7

A fluoride glass was deposited on the substrate while using the apparatus shown in Fig. 2. $ZrBr_4$ and Ba(pivaloyltrifluoromethylacetyacetone)$_2$ (hereinafter referred to as $Ba(PTA)_2$) were introduced through the first inlet 1a. $ZrBr_4$ was prepared by sublimating granular zirconium 5 using the heater 4 which was heated to 350 °C, and reacting the sublimated zirconium with bromine gas.

The first feed pipe 7 having the variable leak valve was connected to the container in which granular zirconium 5 was contained. Bromine gas and argon were fed to the container so that $ZrBr_4$ was sublimated by the reaction between Zr and Br_2, and the sublimated $ZrBr_4$ was supplied through the first inlet 1a to the reaction chamber 1 together with argon. The first feed pipe 7 was heated by the heater 9. The content of transition metal impurities in $ZrBr_4$ was suppressed below 1 ppb (part per billion).

In addition, argon acting as the carrier gas was passed through the evaporator 14 saturated with vaporized $Ba(PTA)_2$, which was vaporized from solid $Ba(PTA)_2$ and maintained at 120 °C in the evaporator 14, and through the second feed pipe 11, the variable leak valve and the first inlet 1a to the reaction chamber 1. A fluorine containing gas, hydrogen fluoride HF in this Example, was supplied through the third feed pipe 11 and the second inlet 1b to the reaction chamber 1. The feed rate of HF was adjusted by the variable leak valve. The reaction chamber 1 was maintained at 200 °C and the substrate 3 was maintained at 250 °C.

$ZrBr_4$ and $Ba(PTA)_2$ introduced into the reaction chamber 1 were converted on the substrate 3 to ZrF_4 and BaF_2 as shown by the following reaction equations wherein, (g) indicates the gasesous state, (ad) indicates the adsorbed solid phase and (s) indicates the solid phase.

$$ZrBr_4(g) \rightarrow ZrBr_4(ad)$$
$$Ba(PTA)_2(g) \rightarrow Ba(PTA)_2(ad)$$
$$HF(g) \rightarrow HF(ad)$$
$$ZrBr_4(ad) + 4HF(ad) \rightarrow ZrF_4(s) + 4HBr(ad)$$
$$Ba(PTA)_2(ad) + 2HF(ad) \rightarrow BaF_2(S) + 2(CH_3)_3-C-CO-CH_2-CO-CF_3(ad)$$
$$HBr(ad) \rightarrow HBr(g)$$
$$(CH_3)_3C-CO-CH_2-CO-CF_3(ad) \rightarrow (CH_3)_3C-CO-CH_2-CO-CF_3(g)$$

Since the temperature of the substrate is lower than the glass transition temperature of the formed fluoride glass, ZrF_4 and BaF_2 formed by the above reactions and deposited on the substrate 3 had low mobilities and were frozen in situ on the substrate 3. Accordingly, likewise in the case of quenching, a non-equilibrium state can be realized on the substrate 3. A glass bulk may be prepared by continuing deposition of the fluoride glass for a sufficiently long period of time.

In the reactions described above, fluorinations of $ZrBr_4$ and $Ba(PTA)_2$ by HF take place independently from each other. Therefore, the production rate of ZrF_4 by the reaction of $ZrBr_4-HF$ system and the production rate of BaF_2 by the reaction of $Ba(PTA)_2-HF$ system are maintained also in the reaction system of $ZrBr_4-Ba(PTA)_2-HF$. Accordingly, the ratio of Zr/Ba in the formed glass can be easily controlled.

In this Example, the feed rates were 100 cc/min for $ZrBr_4$, 70 cc/min for $Ba(PTA)_2$ and 150 cc/min for HF. After reacting for 3 hours, a 6.5 mm thick fluoride glass having a composition of $60ZrF_4-40BaF_2$ was formed.

The results of X-ray diffraction, infrared absorption spectroscopy and anaysis of scattering distribution measured by launching a He-Ne laser into the glass block were substantially equivalent to those described in Example 1.

The result of radioactivation analysis of the formed fluoride glass revealed that the content of Fe, Cu, Ni. Co and Cr were less than 1 ppb (part per billion) which was the detection limit of the radioactivation analysis.

Further, by varying the feed rates of the starting materials, fluoride glasses having various compositions were prepared and the thus prepared fluoride glasses were analysed through the fluorescent X-ray analysis. Fluoride glass blocks having varying compositions ranging within $90ZrF_4-10BaF_2$ to $35ZrF-65BaF_2$ were formed. It was hard to prepare fluoride glasses having such compositions by the conventional melting or casting processes.

Example 8

The fluoride glass block prepared by Example 6 and having the composition of $60ZrF_4-40BaF_2$ was cut into a rod shape and the surface thereof was polished to be used as a deposition substrate.

The heating means for glass deposition was changed from heater heating to CO_2 laser heating and the deposition substrate was changed from CaF_2 to the glass rod, the remaining conditions and the apparatus being the same as used in Example 6, whereby a fluoride optical fiber preform was prepared.

The glass rod had an outer diameter of 4 mm and a length of 300mm. Both ends of the glass rod were clamped by chucks, and a glass was deposited on the glass rod while the glass rod was rotated at 60 rpm and moved along its longitudinal direction at a moving speed of 10 mm/min. In order to establish a desired distribution of refractive index, $AlBr_3$ was introduced in addition to $ZrBr_4$ and $Ba(PTA)_2$ to deposite serially on the glass rod substrate a fluoride glass having a composition of $58ZrF_6-37BaF_2-5AlF_3$ which is to be used as a fluoride optical fiber preform. The feed rates of the starting materials were 30 cc/min for $ZrBr_4$, 14 cc/min for $Ba(PTA)_2$ and 2 cc/min for $AlBr_3$. The temperature of the glass rod substrate was 250 °C.

The preform had a diameter of 8mm and a length of 300mm, and the relative refractive index difference between the core and the cladding was 0.7%. The preform was drawn into a fluoride glass optical fiber having a length of 500 meters. The transmission loss of the optical fiber was measured. The minimum loss was 8 db/km at 2.55 um. The result reveals that a long fluoride glass optical fiber having low loss can be produced by the invention.

Example 9

$Ba(DHO)_2$ which is a complex of Ba with 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (DHO), $Zr(HFA)_4$ which is a complex of Zr with hexafluoroacetylacetone (HFA), $La(DHO)_3$ complex, $Al(DHO)_3$ complex and Na(DHO) complex were used as starting materials. These five starting materials, $Ba(DHO)_3$, $Zr(HFA)_4$, $La(DHO)_3$, $Al(DHO)_3$ and Na(DHO), were vaporized and maintained in the gaseous state by heating, respectively, at 210 °C, 60 °C, 180 °C, 70 °C and 190 °C, and supplied into the reaction chamber while using argon as the carrier gas. Using the apparatus shown in Fig. 3, aluminium evaporators 9a to 9e charged respectively with complexes $Ba(DHO)_3$, $Zr(HFA)_4$, $La(DHO)_3$, $Al(DHO)_3$ and Na(DHO) were heated and argon gas was introduced into the respective evaporators so that vaporized starting materials were supplied through respective aluminium feed pipes 7a to 7e and the first inlet 1a into the reaction chamber 1.

As a fluorine-containing gas, a mixed gas of HF(95 vol%)-F_2(5 vol%) was supplied through the feed pipe 4 and the second inlet 1b into the reaction chamber 1.

The feed rate of the metal-β-ketonate complexes and the mixed gas could be adjusted by means of mass flow controllers.

Using heaters, the feed pipes 7a to 7e were maintained at 215 °C, 65 °C, 185 °C, 75 °C and 195 °C respectively in order to prevent condensation of the respective gase contained therein.

The metal-β-diketonate complexes introduced into the reaction chamber 1 were converted to fluorides in a form of fine glass particles due to homogeneous nucleation in the gaseous phase.

In fluorination by HF of the metal-β-diketonate complexes, $Ba(DHO)_3$, $Zr(HFA)_4$, $La(DHO)_3$, $Al(DHO)_3$ and Na(DHO), the respective complexes were fluorinated independently so that the composition of the resultant glass could be easily controlled by varying the feed rates of the respective complexes.

In this Example, reaction was continued for 2 hours while maintaining the feed rates of the starting materials at 50 cc/min for $Ba(DHO)_3$, 100 cc/min for $Zr(HFA)_4$, 10 cc/min for $La(DHO)_3$, 7.5 cc/min for $Al(DHO)_3$ and 7.5 cc for Na(DHO) and 15 cc/min for $HF-F_2$ mixture gas. The composition of the fine glass particles was $53ZrF_4-20BaF_2-4LaF_3-3AlF_3-22NaF$, and the formed product was deposited on the interior wall of the cylindrical glass tube 3. The composition of the cylindrical glass was $39.7ZrF_4-13.3HfF_4-18.0BaF_2-4.0LaF_3-3.0AlF_3-22NaF$.

Fig. 12 shows schematically an apparatus used for collapsing a cylindrical tube having its interior wall deposited with fine glass particles.

Both ends of the cylindrical glass tube 3, having fine glass particles deposited over the interior wall by the process as aforemention d, were allowed to contact an aluminum connector 18, and the internal pressure of the cylindrical tube was controlled to 66.66 KPa (500 mmHg) while introducing F_2 gas from the downside as viewed in Fig. 12 and evacuating by a rotary pump (R.P., not shown) from the upside as viewed in Fig. 12. The temperature was set to 200 °C by a heater 12, and processing was continued for 2 hours. The temperature was then raised to 280 °C to collapse the tube 3 entirely, whereby a preform was obtained.

In this Example, a cylindrical tube of fluoride glass having an outer diameter of 12 mm, an inner diameter of 8 mm and a length of 150 mm was used. However, by increasing the diameter of the glass tube 3 used as the substrate, the size of the preform can be further increased. For instance, a cylindrical tube 3 having an outer diameter of 20mm, an inner diameter of 12 mm and a length of 300 mm was used as the substrate and deposition of fine glass particles was effected for 3 to 5 hours, followed by collapsing, whereby a large size collapsed preform was obtained.

In collapsing the cylindrical tube 3, having deposited therein fine glass particles 20, it is preferable that the temperature is maintained within the range of from 50°C to 500°C, although the temperature may be changed corresponding to the composition of the fluoride glass.

Fluorine gas was used in this Example to remove oxide impurites absorbed on the surface of the deposited particles. However, other halogen-containing gases, such as gaseous compounds of fluorine or chlorine with hydrogen, carbon, nitrogen, boron, sulfur and silicon or mixture of at least two of said gases, may also be used for this purpose.

Example 10

The collapsed preform prepared by Example 9 was placed in a drawing furnace filled with an inert gas, and drawn at 285°C into a fluoride glass optical fiber.

A He-Ne laser was launched into the thus produced fluoride glass optical fiber and the scattered light intensity along the fiber axis was measured. For comparison purpose, the scattering distribution of a fluoride fiber produced by the convetional casting process was also measured. The results are shown in Fig. 13.

It is apparently seen from Fig. 13 that scattering can be significantly reduced in fluoride glass produced according to the process of the present invention. In the process of the present invention, vaporization of the starting materials for the glass and deposition or synthesis of glass particles can be effected by a single step. As an advantageous result of the single step processing, fine glass particles containing no oxide impurites can be produced. The oxide impurities adsorbed on the surface of the deposited mass could be removed by treatment with a fluorine-containing gas, without exposure to the outside atmosphere, whereby a preform is obtained.

The transmission loss of the produced optical fiber was measured. The result is shown in Fig. 14. The minimum loss, at a wavelength of 2.55 µm, of the produced optical fiber was 0.9 dB/km which was not attainable by the conventional technology, for such a fiber length.

Example 11

The procedure as described in Example 9 was followed so that fine particles of a fluoride glass constituting a core composition was deposited over the interior wall of a glass tube 3 constituting the cladding glass composition. The glass tube was then placed in a drawing furnace where it was processed at 200°C for an hour in a flowing F_2 gas stream. Thereafter, the internal pressure was set to 93.33 KPa (700 Torr) by evacuating the interior of the tube from the upper end which was connected to a rotary pump. The drawing furnace was heated to 285°C and the glass tube was elongated simultaneously with the collapsing operation to obtain a fluoride optical fiber having a minimum transmission loss of 0.7 dB/km at 2.55 µm. A long fluoride glass optical fiber having a low transmission loss factor was produced in this Example, by simultaneous drawing and collapsing. Similar effects can be obtained by using Cl_2, HF, HCl, BF_3, SF_6, SiF_4, CF_4 or a mixture thereof in place or in addition to F_2 in the processing step prior to the drawing step.

Example 12

A fluoride optical fiber was produced as in Example 10 except that a Teflon (Trade name) fluorethylene pipe (FEP) tube was used in place of the glass tube.

In addition to the metal-β-diketonate complexes used in Example 10, $Hf(HFA)_4$ was used. The feed rates of respective metal-β-diketonate complexes are set out below:

$Zr(HFA)_4$ --- 87.5 cc/min
$Hf(HFA)_4$ --- 12.5 cc/min
$Ba(DHO)_2$ --- 45 cc/min
$La(DHO)_3$ --- 10 cc/min
$Al(DHO)_3$ --- 7.5 cc/min
Na(DHO) --- 40 cc/min

The flow rate of HF-F_2 was 100 cc/min. Glass particles were deposited over the interior wall of the FEP

(fluoroethylene pipe) tube. The deposited fine glass particles had a composition of 39.7ZrF_4 − 13.3HfF_2 − 18.0BaF_2 − 4.0LaF_2 − 3.0AlF_3 − 22NaF. Thereafter, feeding of $Hf(HFA)_4$ was stopped. Then, in order to form a core layer, feed rates of respective metal − β − diketonate complexes were adjusted to the rates as set out below:

$Zr(HFA)_4$ - - - 100 cc/min
$Ba(DHO)_2$ - - - 50 cc/min
$La(DHO)_3$ - - - 10 cc/min
$Al(DHO)_3$ - - - 7.5 cc/min
Na(DHO) - - - 40 cc/min

The deposition was effected for 2 hours with the flow rates of the starting materials as set out above and the flow rate of HF − F_2 was set to 100 cc/min. The composition of the formed glass was 53ZrF_4 − 20BaF_2 − 4LaF_3 − 3AlF_3 − 22NaF.

The fluoride glass deposited on the interior wall of the FEP (fluoroethylene pipe) tube, the cladding layer and the core layer were drawn as described in Example 10. The thus produced fluoride glass optical fiber covered by a Teflon FEP had a long size and a low transmission loss. The core/cladding diameter ratio may be freely changed by varying the times for deposition of fine fluoride glass particles for the formation of core and cladding layers.

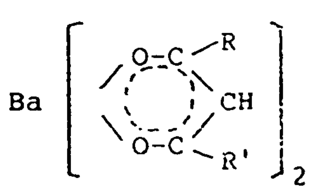
Example 13

The process of Example 12 was followed, except that aluminium was coated by vapor deposition over the interior wall of a tube made of an oxide glass having a composition of 22B_2O_3 − 48PbO − 30Tl_2O_3. This oxide glass tube was used in place of the FEP tube as used in Example 12. The procedure of this example, as in Example 12, led to deposition of fluoride glasses followed by collapsing and drawing to produce an fluoride glass optical fiber having an appreciable length and low transmission loss. The cylindrical tube used as the substrate on which fine particle of fluoride glass is deposited, may be a single layer or multi − layered cylindrical tube made of any of glasses, metal and organic polymers.

Claims

1. A process for preparing a fluoride glass containing barium comprising the step of introducing a gaseous mixture into a reaction system containing a substrate to react the ingredients of said gaseous mixture in a gaseous phase or on said substrate to deposit a metal fluoride to form a fluoride glass, said gaseous mixture comprising a gaseous or vaporizable compound of the metallic element constituting said fluoride glass, the gaseous or vaporizable compound serving as a first starting material, characterized in that said gaseous mixture further comprises

   a barium β − diketonate complex serving as a second starting material which is a complex of barium and any one of 3,5 − pentadione, 2,2,6,6 − tetramethyl − 3,5 − heptanedione, 2,2 − dimethyl − 3,5 − octanedione and 1,1,1,5,5,5 − hexafluoro − 2,4 − pentanedione or a complex represented by the following general formula (1) of:



------------ (1)

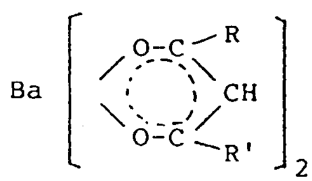
   wherein R is an alkyl group having 1 to 7 carbon atoms, R' is a substituted alkyl group having fluorine atoms substituting hydrogen atoms and represented by C_nF_{2n+1} where n is an integer of from 1 to 3; and

2. A process for preparing a fluoride glass according to claim 1, wherein said gaseous mixture further comprises a fluorine − containing gas serving as a fluorinating agent.

3. A process for preparing a fluoride glass containing barium comprising the step of introducing a gaseous mixture into a reaction system containing a cylindrical substrate to react the ingredients of said

gaseous mixture in a gaseous phase or on the interior wall of said substrate to deposit a coating or fine particles of a m tal fluoride to form a fluoride glass, said gaseous mixture comprising a gaseous or vaporizable compound of the metallic element constituting said fluoride glass, the gaseous or vaporizable compound serving as a first starting material, characterized in that said gaseous mixture further comprises

a barium β-diketonate complex serving as a second starting material which is a complex of barium and any one of 3,5-pentadione, 2,2,6,6-tetramethyl-3,5-heptanedione, 2,2-dimethyl-3,5-octanedione and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione or a complex represented by the following general formula (1) of:



----------- (1)

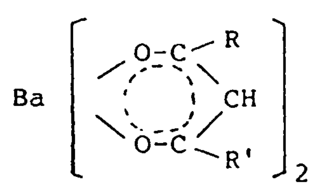
wherein R is an alkyl group having 1 to 7 carbon atoms, R' is a substituted alkyl group having fluorine atoms substituting hydrogen atoms and represented by C_nF_{2n+1} where $\underline{n}$ is an integer of from 1 to 3; and

a fluorine-containing gas serving as a fluorinating agent;

the process being further characterized in that said cylindrical substrate containing therein deposited coating or fine particles of a fluoride glass is heated to solidify the same to form a preform for opticl fibers.

4. A process for preparing a fluoride glass containing barium comprising the step of introducing a gaseous mixture into a reaction system containing a rod-like glass substrate to react the ingredients of said gaseous mixture in a gaseous phase or on the surface of said substrate to deposit a layer or fine particles of fluoride glass on the surface of said substrate, said gaseous mixture comprising a gaseous or vaporizable compound of the metallic element constituting said fluoride glass, the gaseous or vaporizable compound serving as a first starting material, characterized in that said gaseous mixture further comprises

a barium β-diketonate complex serving as a second starting material which is a complex of barium and any one of 3,5-pentadione, 2,2,6,6-tetramethyl-3,5-heptanedione, 2,2-dimethyl-3,5-octanedione and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione or a complex represented by the following formula (1) of:



----------- (1)

wherein R is an alkyl group having 1 to 7 carbon atoms, R' is a substituted alkyl group having fluorine atoms substituting hydrogen atoms and represented by C_nF_{2n+1} where $\underline{n}$ is an integer of from 1 to 3; and

a fluorine-contained gas serving as a fluorinating agent;

the process being further characterized in that said rod-like glass substrate containing thereon a lyer or deposited fine particles of a fluoride glass is heated to solidify the same to form a preform for optical fibers.

5. A process according to any of claims 1 to 4, wherein said gaseous or vaporizable compound is at least one of metal halides, organic metal compounds and metal β-diketonate complexes.

6. A process according to claim 5, wherein said metal halides are halides of metallic elements of Ia, IIa, IIIa, IVa, Va, Ib, IIb, IIIb, IVb, Vb, VIb, VIIb and VIIIb groups.

7. A process - according to any of claims 1 to 4, wherein said first starting material is $Al(CH_3)_3$ or $Al-(C_2H_5)_3$.

8. A process according to any of claims 1 to 4, wherein said β-diketonate is any one of 5,5,5-trifluoro-2,4-pentanedione, 2,2-dimethyl-6,6,6-trifluoro-3,5-hexanedione, 2.2.-dimethyl-6,6,7,7,7-pentafluoro-3,5-heptanedione and 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione.

9. A process according to any of claims 1 to 4, wherein said metallic element constituting said fluoride glass is one or more of Ba, Zr, Ca, Al, Na, Li, Hf, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, In, Sn, Pb, Sb, Bi, Zn, Cd, Ti. Th, Nb, Ta, Mo or Mn.

10. A process according to any of claims 2, 3 and 4, wherein said fluorine-containing gas is fluorine gas or a gaseous compound of fluorine with any one or more of hydrogen, halogens, carbon, nitrogen, boron, silicon and sulfur.

11. A process according to any of claims 1 to 4, wherein said substrate consists of fluoride glass, CaF_2, metal, oxide glass, polymer or multi-layer thereof.

12. A process according to any of claims 1 to 4, wherein said fluoride glass is any of BaF_2-ZrF_4 system, BaF_2-HfF_4 system or BaF_2-AlF_3 system glasses.

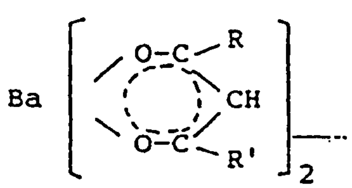
13. A process according to claim 3 or 4, wherein hydrogen fluoride gas serving as a fluorinating agent is added to the gaseous flow in addition to said first starting material and said second starting material.

14. A process according to claim 3, wherein the fluoride glass deposited on the interior wall of said cyclidrical substrate is heated in an environment of fluorine or clorine, or gaseous compounds of fluorine or chlorine with any one or more of hydrogen, carbon, nitrogen, boron, sulfur and silicon, or mixture of at least two of said gases.

15. A process according to claim 3 or 4, further comprising the step of drawing said preform for optical fiber to form an drawn optical fluoride fiber.

Patentansprüche

1. Ein Verfahren zur Herstellung eines Barium enthaltenden Fluoridglases aufweisend den Schritt der Einleitung eines Gasgemisches in ein Reaktionssystem, das ein Substrat enthält zum Reagieren der Bestandteile des genannten Gasgemisches in einer gasförmigen Phase oder auf genanntem Substrat, um ein Metallfluorid zum Bilden eines Fluoridglases abzulagern, wobei das genannte Gasgemisch eine gasförmige oder verdampfbare Verbindung des metallischen Elements aufweist, das ein Bestandteil des Fluoridglases ist, wobei die gasförmige oder verdampfbare Verbindung als ein erstes Startmaterial dient, dadurch gekennzeichnet, daß desweiteren das genannte Gasgemisch
einen als zweites Startmaterial dienenden Barium-β-Diketonatkomplex enthält, der ein Komplex ist aus Barium und einem Glied aus der Gruppe 3,5-Pentadion, 2,2,6,6-Tetramethyl-3,5-Heptandion, 2,2-Dimethyl-3,5-Octandion und 1,1,1,5,5,5-Hexafluoro-2,4-Pentandion oder ein Komplex, der durch folgende allgemeine Formel (1) dargestellt wird:

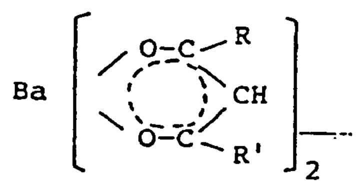


----------- (1)

worin R eine Alkylgruppe mit 1 bis 7 Kohlenstoffatomen ist, R' eine substituierte Alkylgruppe mit Fluoratomen ist, die die Wasserstoffatome ersetzen, und die dargestellt wird durch C_nF_{2n+1}, wobei n eine ganz Zahl von 1 bis 3 ist.

2. Ein Verfahren zur Herstellung eines Fluoridglases nach Anspruch 1, bei dem das genannte Gasgemisch außerdem ein fluorhaltiges Gas enthält, das als fluorisierendes Agens dient.

3. Ein Verfahren zur Herstellung eines Barium enthaltenden Fluoridglases aufweisend den Schritt der Einleitung eines Gasgemisches in ein Reaktionssystem, das ein zylinderförmiges Substrat enthält zum Reagieren der Bestandteile des genannten Gasgemisches in einer gasförmigen Phase oder auf der Innenwand des genannten Substrats, um einen Überzug oder feine Partikel eines Metallfluorids zum Bilden eines Fluoridglases abzulagern, wobei das genannte Gasgemisch eine gasförmige oder verdampfbare Verbindung des metallischen Elements aufweist, das ein Bestandteil des Fluoridglases ist, wobei die gasförmige oder verdampfbare Verbindung als ein erstes Startmaterial dient, dadurch gekennzeichnet, daß desweiteren das genannte Gasgemisch
einen als zweites Startmaterial dienenden Barium-β-Diketonatkomplex enthält, der ein Komplex ist aus Barium und einem Glied aus der Gruppe 3,5-Pentadion, 2,2,6,6-Tetramethyl-3,5-Heptandion, 2,2-Dimethyl-3,5-Octandion und 1,1,1,5,5,5-Hexafluoro-2,4-Pentandion oder ein Komplex, der durch folgende allgemeine Formel (1) dargestellt wird:

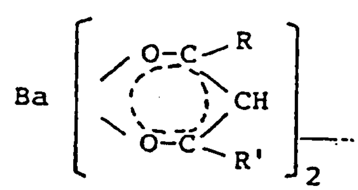


(1)

worin R eine Alkylgruppe mit 1 bis 7 Kohlenstoffatomen ist, R' eine substituierte Alkylgruppe mit Fluoratomen ist, die die Wasserstoffatome ersetzen, und die dargestellt wird durch C_nF_{2n+1}, wobei n eine ganze Zahl von 1 bis 3 ist; und ein fluorhaltiges Gas, das als fluorisierendes Agens dient;

wobei das Verfahren weiterhin dadurch gekennzeichnet ist, daß das zylinderförmige Substrat, in dem sich der abgelagerte Überzug oder feine Partikel eines Fluoridglases befinden, erhitzt wird, damit dieses zur Bildung einer Vorform für optische Fibern erstarrt.

4. Ein Verfahren zur Herstellung eines Barium enthaltenden Fluoridglases aufweisend den Schritt der Einleitung eines Gasgemisches in ein Reaktionssystem, das ein stangenförmiges Glassubstrat enthält zum Reagieren der Bestandteile des genannten Gasgemisches in einer gasförmigen Phase oder auf der Oberfläche des genannten Substrats, um eine Schicht oder feine Partikel eines Metallfluorids an der Oberfläche des genannten Substrats abzulagern, wobei das genannte Gasgemisch eine gasförmige oder verdampfbare Verbindung des metallischen Elements aufweist, das ein Bestandteil des Fluoridglases ist, wobei die gasförmige oder verdampfbare Verbindung als ein erstes Startmaterial dient, dadurch gekennzeichnet, daß desweiteren das genannte Gasgemisch
einen als zweites Startmaterial dienenden Barium-β-Diketonatkomplex enthält, der ein Komplex ist aus Barium und einem Glied aus der Gruppe 3,5-Pentadion, 2,2,6,6-Tetramethyl-3,5-Heptandion, 2,2-Dimethyl-3,5-Octandion und 1,1,1,5,5,5-Hexafluoro-2,4-Pentandion oder ein Komplex, der durch folgende allgemeine Formel (1) dargestellt wird:



(1)

worin R eine Alkylgruppe mit 1 bis 7 Kohlenstoffatomen ist, R' eine substituierte Alkylgruppe mit Fluoratomen ist, die die Wasserstoffatome ersetzen, und di dargestellt wird durch C_nF_{2n+1}, wobei n eine ganze Zahl von 1 bis 3 ist; und ein fluorhaltiges Gas, das als fluorisierendes Agens dient;

wobei das Verfahren weiterhin dadurch gekennzeichnet ist, daß das stangenförmige Glassubstrat, auf dem sich eine Schicht oder abgelagerte feine Partikel eines Fluoridglases befinden, erhitzt wird, damit dieses zur Bildung einer Vorform für optische Fibern erstarrt.

5. Ein Verfahren nach einem der Ansprüche 1 bis 4, bei dem die genannte gasförmige oder verdampfbare Verbindung mindestens eine aus der Gruppe der Metallhalogenide, organischen Metallverbindungen und Metall - β - Diketonatkomplexe ist.

6. Ein Verfahren nach Anspruch 5, bei dem die genannten Metallhalogenide Halogenide der metallischen Elemente der Ia, IIa, IIIa, IVa, Va, Ib, IIb, IIIb, IVb, Vb, VIb, VIIb und VIIIb Gruppen sind.

7. Ein Verfahren nach einem der Ansprüche 1 bis 4, bei dem das genannte erste Startmaterial entweder $Al(CH_3)_3$ oder $Al(C_2H_5)_3$ ist.

8. Ein Verfahren nach einem der Ansprüche 1 bis 4, bei dem das genannte β - Diketonat eines aus der Gruppe 5,5,5 - Trifluoro - 2,4 - Pentandion, 2,2 - Dimethyl - 6,6,6 - Trifluoro - 3,5 - Hexandion, 2.2. - Dimethyl - 6,6,7,7,7 - Pentafluoro - 3,5 - Heptandion und 2,2 - Dimethyl - 6,6,7,7,8,8,8 - Heptafluoro - 3,5 - Octandion ist.

9. Ein Verfahren nach einem der Ansprüche 1 bis 4, bei dem das genannte metallische Element, welches Bestandteil des Fluoridglases ist eines oder mehrere der Elemente aus der Gruppe Ba, Zr, Ca, Al, Na, Li, Hf, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, In, Sn, Pb, Sb, Bi, Zn, Cd, Ti, Th, Nb, Ta, Mo oder Mn ist.

10. Ein Verfahren nach einem der Ansprüche 2, 3 und 4, bei dem das genannte fluorhaltige Gas ein Fluorgas ist oder eine gasförmige Verbindung aus Fluor mit einem oder mit mehreren der folgenden Stoffe Wasserstoff, Halogene, Kohlenstoff, Stickstoff, Bor, Silizium und Schwefel.

11. Ein Verfahren nach einem der Ansprüche 1 bis 4, bei dem das genannte Substrat aus Fluoridglas, CaF_2, Metall, Oxydglas, Polymer oder mehreren Lagen davon besteht.

12. Ein Verfahren nach einem der Ansprüche 1 bis 4, bei dem das genannte Fluoridglas eines der Gläser der Systeme $BaF_2 - ZrF_4$, $BaF_2 - HfF_4$ oder $BaF_2 - Alf_3$ ist.

13. Ein Verfahren nach Anspruch 3 oder 4, bei dem ein Hydrogenfluoridgas, das als fluorisierendes Agens dient, dem gasförmigen Strom zusätzlich zu dem genannten ersten Startmaterial und dem genannten zweiten Startmaterial hinzugefügt wird.

14. Ein Verfahren nach Anspruch 3, bei dem das Fluoridglas, das an der Innenwand des zylinderförmigen Substrates abgelagert ist, in einer Umgebung von Fluor oder Chlor oder gasförmigen Verbindungen aus Fluor oder Chlor mit einem oder mit mehreren Elementen aus der Gruppe Wasserstoff, Kohlenstoff, Stickstoff, Bor, Schwefel und Silizium oder in einer Mischung aus mindestens zwei dieser genannten Gase erhitzt wird.

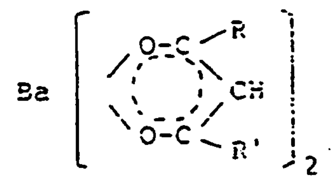
15. Ein Verfahren nach Anspruch 3 oder 4, das außerdem den Schritt des Ziehens der genannten Vorform für optische Fibern umfaßt, um eine gezogene optische Fluoridfiber zu erstellen.

Revendications

1. Procédé pour la production d'un verre de fluorures contenant du baryum, comprenant l'étape d'introduction d'un mélange gazeux dans un système réactionnel contenant un support, pour faire réagir les composants dudit mélange gazeux, dans la phase gazeuse ou sur ledit support, afin de déposer des fluorures métalliques pour la formation d'un verre de fluorures, ledit mélange gazeux comprenant un composé gazeux ou vaporisable de l'élément métallique constituant ledit verre de fluorures, le composé gazeux ou vaporisable servant de premier produit de départ, caractérisé en ce que ledit

mélange gazeux comprend en outre

un complexe de baryum-β-dicétonate servant de second produit de départ, qui est un complexe de baryum et d l'une quelconque parmi la 3,5-pentanedione, la 2,2,6,6-tétraméthyl-3,5-heptane-dione, la 2,2-diméthyl-3,5-octanedione et la 1,1,1,5,5,5-hexafluoro-2,4-pentanedione ou un complexe représenté par la formule générale (1) suivante:

 ----------- (1)

dans laquelle

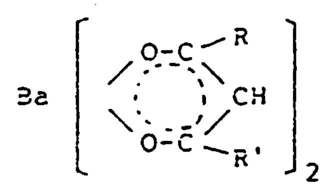
R est un groupe alkyle ayant de 1 à 7 atomes de carbone,

R' est un groupe alkyle substitué comportant des atomes de fluor substituant des atomes d'hydrogène, et représenté par C_nF_{2n+1}, n étant un nombre entier allant de 1 à 3.

2. Procédé pour la production d'un verre de fluorures selon la revendication 1, dans lequel ledit mélange gazeux comprend en outre un gaz fluoré servant d'agent de fluoration.

3. Procédé pour la production d'un verre de fluorures contenant du baryum, comprenant l'étape d'intro-duction d'un mélange gazeux dans un système réactionnel contenant un support cylindrique, pour faire réagir les composants dudit mélange gazeux dans la phase gazeuse ou sur la paroi interne dudit support, afin de déposer un revêtement de fines particules d'un fluorure métallique pour la formation d'un verre de fluorures, ledit mélange gazeux comprenant un composé gazeux ou vaporisable de l' élément métallique constituant ledit verre de fluorures, le composé gazeux ou vaporisable servant de premier produit de départ, caractérisé en ce que ledit mélange gazeux comprend en outre

un complexe de baryum-β-dicétonate servant de second produit de départ, qui est un complexe de baryum et de l'une quelconque parmi la 3,5-pentanedione, la 2,2,6,6-tétraméthyl-3,5-heptane-dione, la 2,2-diméthyl-3,5-octanedione et la 1,1,1,5,5,5-hexafluoro-2,4-pentanedione ou un complexe représenté par la formule générale (1) suivante:

 ----------- (1)

dans laquelle

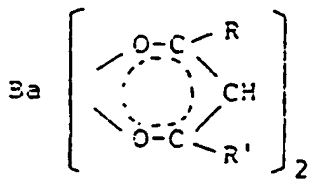
R est un groupe alkyle ayant de 1 à 7 atomes de carbone,

R' est un groupe alkyle substitué comportant des atomes de fluor substituant des atomes d'hydrogène et représenté par C_nF_{2n+1}, n étant un nombre entier allant de 1 à 3; et

un gaz fluoré servant d'agent de fluoration; le procédé étant en outre caractérisé en ce que ledit support cylindrique, contenant un revêtement ou de fines particules de verre de fluorures déposés sur celui-ci, est chauffé pour sa solidification, pour la formation d'une préforme pour fibres optiques.

4. Procédé pour la production d'un verre de fluorures contenant du baryum, comprenant l'étape d'intro-duction d'un mélange gazeux dans un système réactionnel contenant un support en verr de type baguette, pour faire réagir les composants dudit mélange gazeux dans la phase gazeuse ou sur la surface dudit support, afin de déposer une couche ou de fines particules de verre de fluorures sur la surface dudit support, ledit mélange gazeux comprenant un composé gazeux ou vaporisable de l'élément métallique constituant ledit verre de fluorures, le composé gazeux ou vaporisable servant de premier produit de départ, caractérisé en ce que ledit mélange gazeux comprend en outre

un complexe de baryum - β - dicétonate servant de second produit de départ, qui est un complexe de baryum et de l'une quelconque parmi la 3,5 - pentanedione, la 2,2,6,6 - tétraméthyl - 3,5 - heptanedione, la 2,2 - diméthyl - 3,5 - octanedione et la 1,1,1,5,5,5 - hexafluoro - 2,4 - pentanedione ou un complexe représenté par la formule générale (1) suivante:



(1)

dans laquelle

R est un groupe alkyle ayant de 1 à 7 atomes de carbone,

R' est un groupe alkyle substitué comportant des atomes de fluor substituant des atomes d'hydrogène et représenté par C_nF_{2n+1}, n étant un nombre entier allant de 1 à 3; et

un gaz fluoré servant d'agent de fluoration; le procédé étant en outre caractérisé en ce que ledit support en verre de type baguette, contenant une couche ou de fines particules déposées d'un verre de fluorures, est chauffé, pour sa solidification, pour la formation d'une préforme pour fibres optiques.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit composé gazeux ou vaporisable est au moins l'un parmi des halogénures métalliques, des composés organométalliques et des complexes de métal - β - dicétonate.

6. Procédé selon la revendication 5, dans lequel lesdits halogénures métalliques sont des halogénures d'éléments métalliques des groupes Ia, IIa, IIIa, IVa, Va, Ib, IIb, IIIb, IVb, Vb, VIb, VIIb et VIIIb.

7. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit premier produit de départ est $Al(CH_3)_3$ ou $Al(C_2H_5)_3$.

8. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit β - dicétonate est l'un quelconque parmi la 5,5,5 - trifluoro - 2,4 - pentanedione, la 2,2 - diméthyl - 6,6,6 - trifluoro - 3,5 - hexanedione, la 2,2 - diméthyl - 6,6,7,7,7 - pentafluoro - 3,5 - heptanedione, et la 2,2 - diméthyl - 6,6,7,7,8,8,8 - heptafluoro - 3,5 - octanedione.

9. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit élément métallique constituant ledit verre de fluorures est un ou plusieurs des éléments Ba, Zr, Ca, Al, Na, Li, Hf, Y, La, Ce, Pr, Nd, Pm, Sm Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, In, Sn, Pb, Sb, Bi, Zn, Cd, Ti, Th, Nb, Ta, Mo ou Mn.

10. Procédé selon l'une quelconque des revendications 2, 3 et 4, dans lequel ledit gaz fluoré est le fluor gazeux ou un composé gazeux du fluor avec un ou plusieurs éléments parmi l'hydrogène, des halogènes, le carbone, l'azote, le bore, le silicium et le soufre.

11. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit support est constitué de verre de fluorures, CaF_2, métal, verre d'oxydes, polymères ou d'une multicouche de ceux - ci;

12. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit verre de fluorures est l'un quelconque de verres de type $BaF_2 - ZrF_4$, $BaF_2 - HfF_4$ ou $BaF_2 - AlF_3$.

13. Procédé selon la revendication 3 ou 4, dans lequel le gaz fluorhydrique servant d'agent de fluoration est ajouté au courant gazeux en plus dudit premier produit de départ et dudit second produit de départ.

14. Procédé selon la revendication 3, dans lequel le gaz fluoré déposé sur la paroi interne dudit support cylindrique est chauffé dans un environnement de fluor ou de chlore, ou de composés gazeux du fluor ou du chlore avec un ou plusieurs éléments parmi l'hydrogène, le carbone, l'azote, le bore, le soufre et le silicium, ou un mélange d'au moins deux desdits gaz.

15. Procédé la revendication 3 ou 4, comprenant n outre l'étape d'étirage de ladite préforme en une fibre optique, pour la formation d'une fibre optique de fluorures étirée.

FIG.1

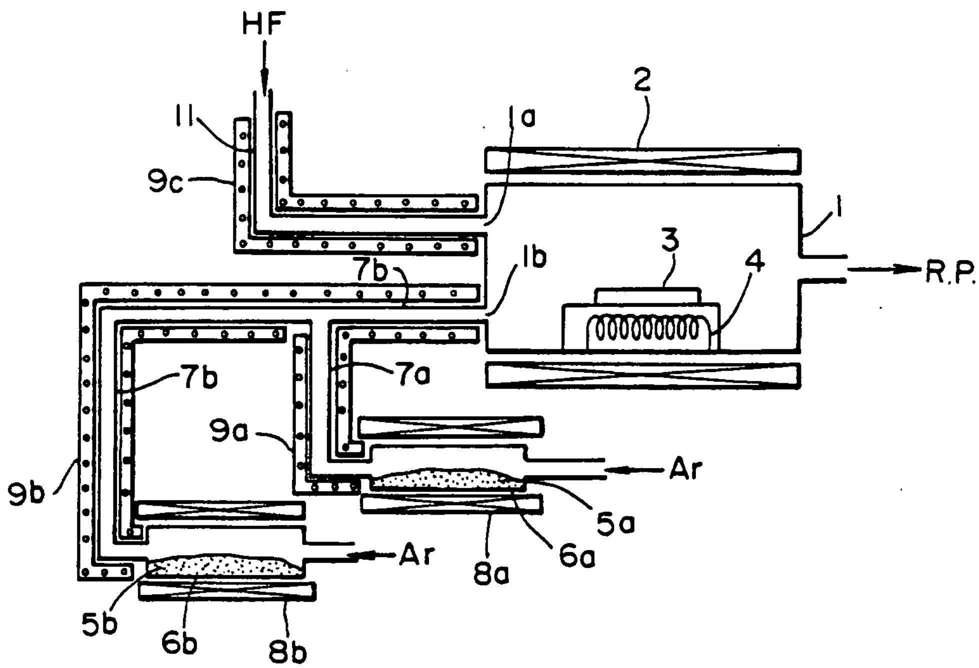

HF
2
11
1a
9c
1
3
4
1b
7b
R.P.
7b
7a
9a
Ar
9b
5a
Ar
6a
8a
5b
6b
8b

FIG.2

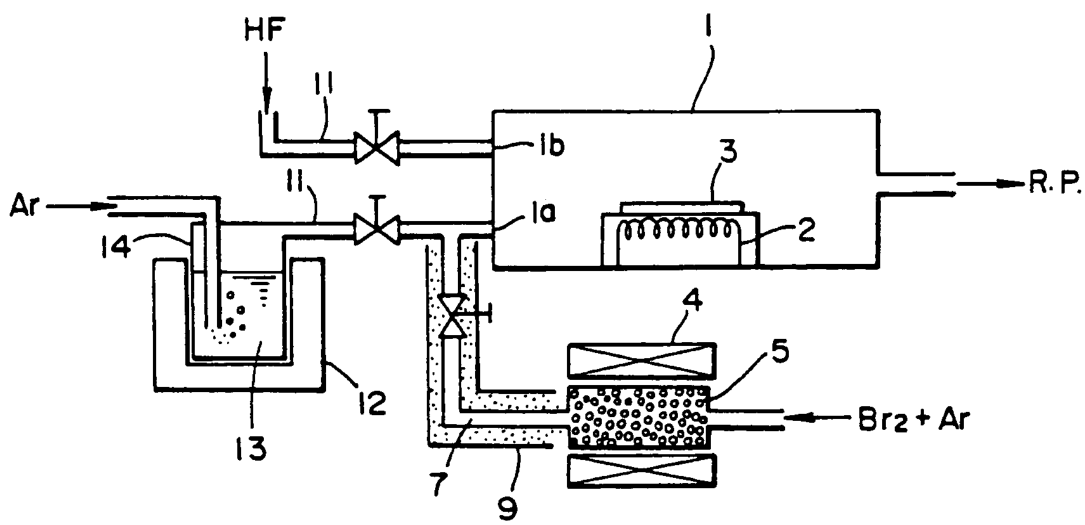

HF
1
11
1b
3
Ar
11
R.P.
14
1a
2
4
5
Br2 + Ar
12
13
7
9

FIG.3

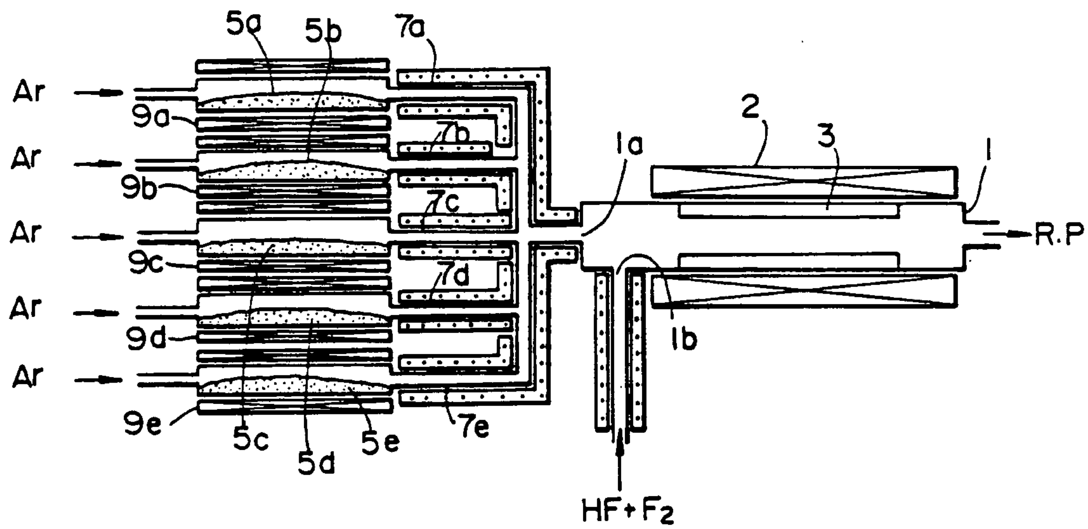

5a
5b
7a
Ar
9a
7b
Ar
9b
7c
Ar
9c
7d
Ar
9d
Ar
9e
5c
5d
5e
7e
2
3
1a
1
R.P
1b
HF+F2

FIG.4

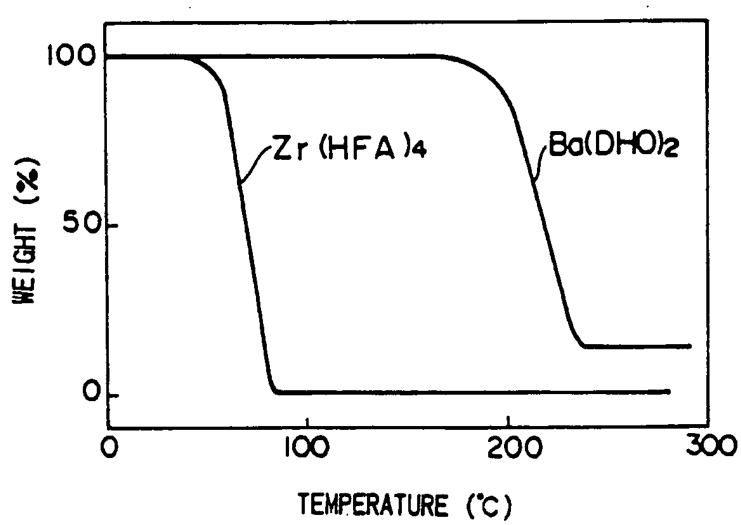

100
50
0
WEIGHT (%)
Zr (HFA)4
Ba(DHO)2
0
100
200
300
TEMPERATURE (°C)

FIG.5

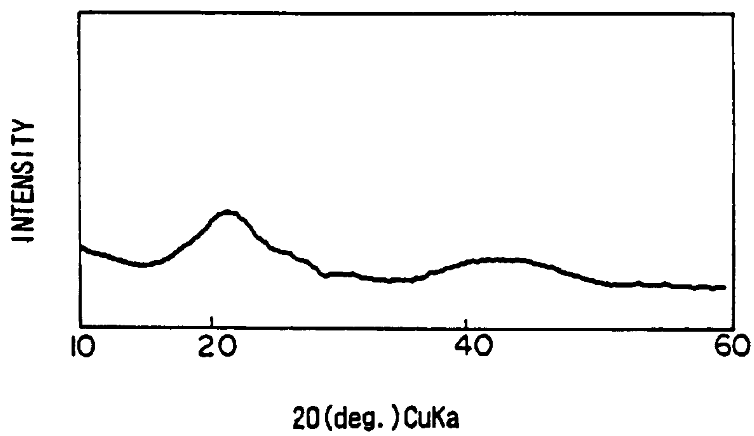

INTENSITY
10
20
40
60
2θ(deg.)CuKa

FIG.6

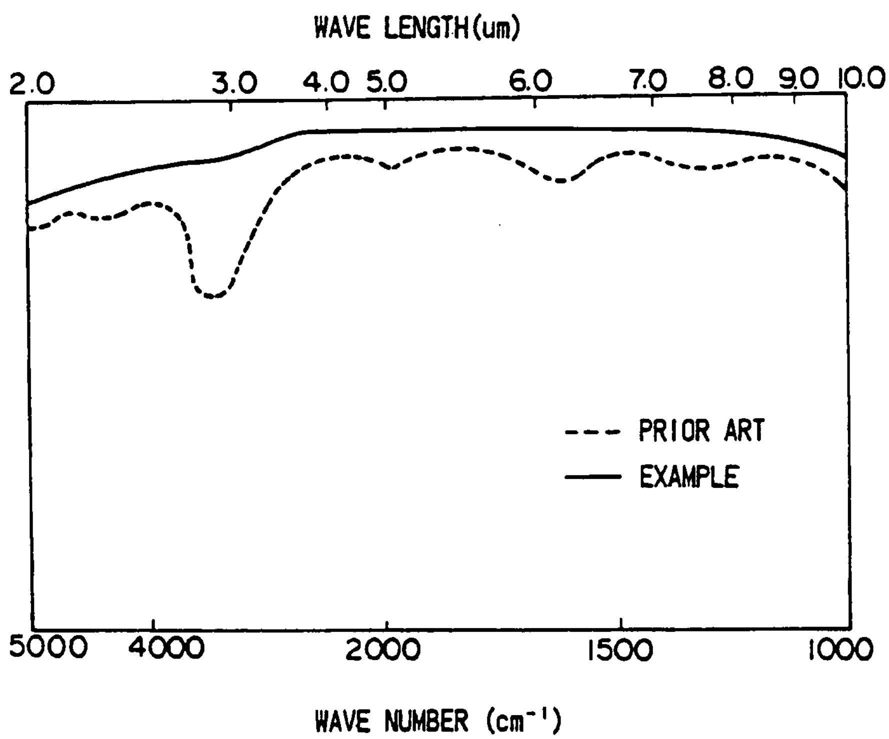

WAVE LENGTH(um)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
PRIOR ART
EXAMPLE
5000
4000
2000
1500
1000
WAVE NUMBER (cm⁻¹)

FIG.7

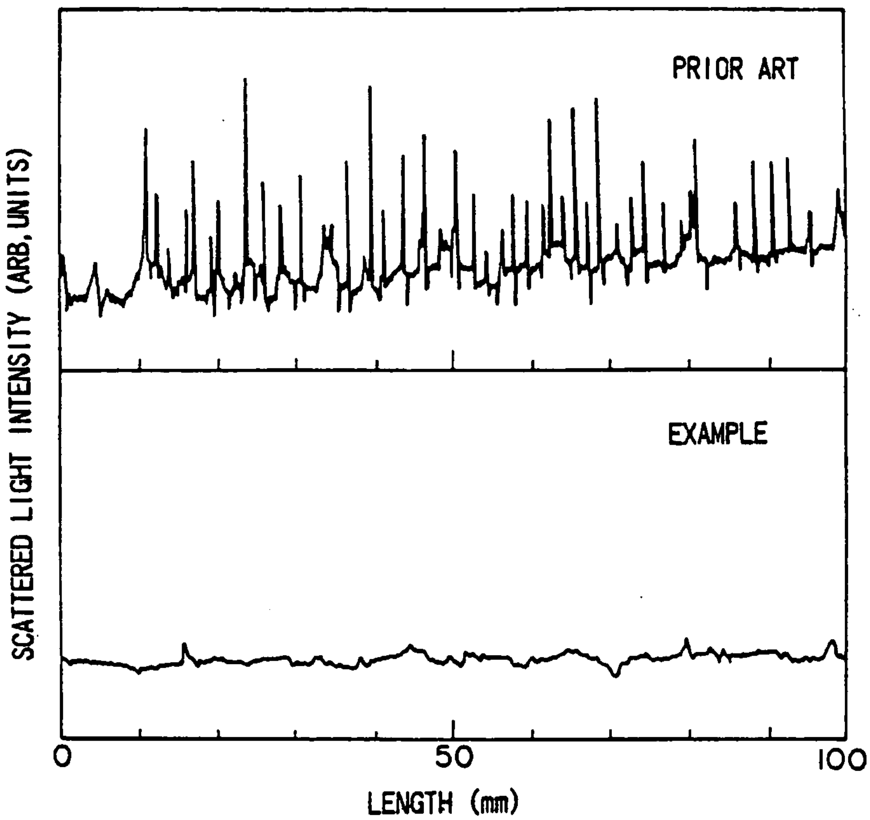

PRIOR ART
EXAMPLE
SCATTERED LIGHT INTENSITY (ARB, UNITS)
0
50
100
LENGTH (mm)

FIG.8

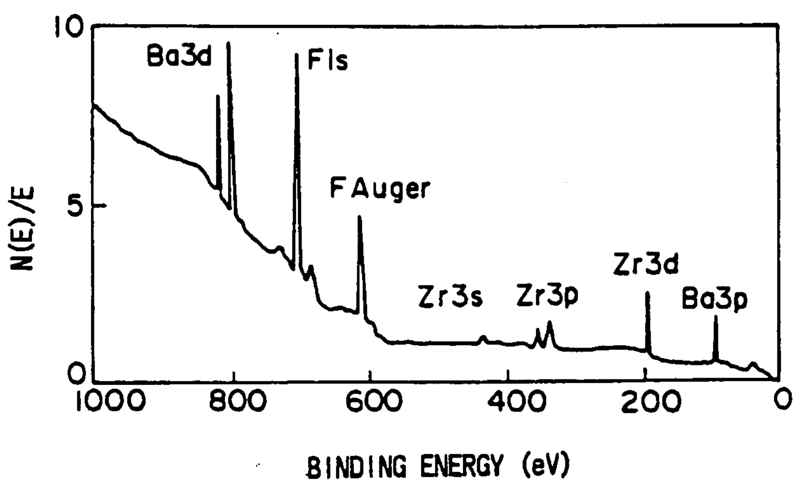

10
5
0
Ba3d
F1s
F Auger
Zr3s
Zr3p
Zr3d
Ba3p
N(E)/E
1000
800
600
400
200
0
BINDING ENERGY (eV)

FIG. 9

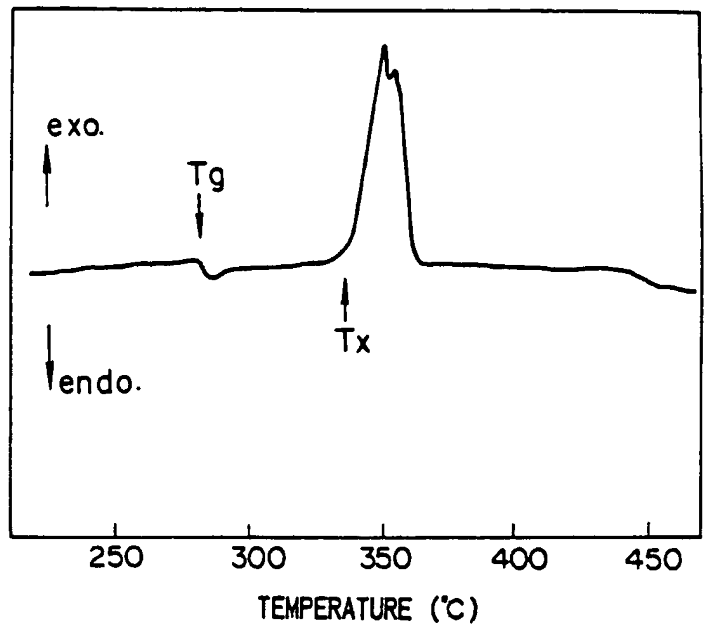

exo.
Tg
Tx
endo.
250
300
350
400
450
TEMPERATURE (°C)

FIG. 10

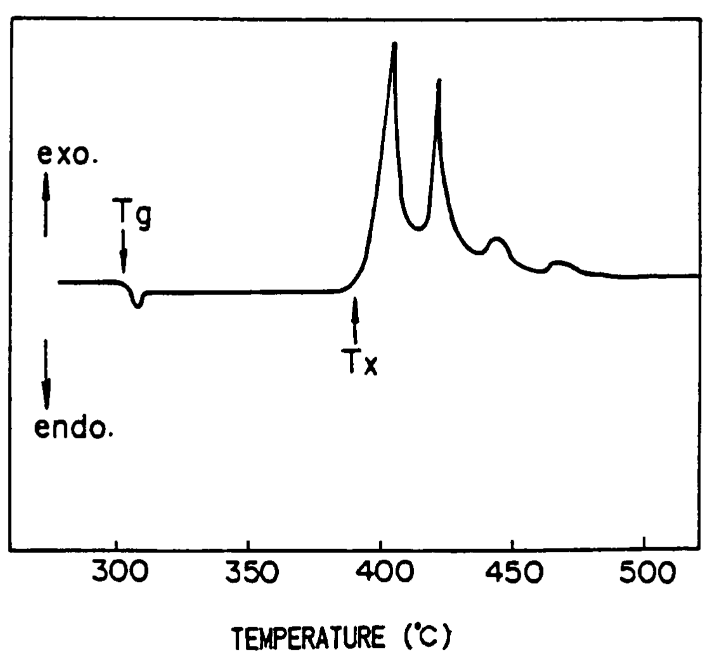

exo.
Tg
Tx
endo.
300
350
400
450
500
TEMPERATURE (°C)

FIG.11

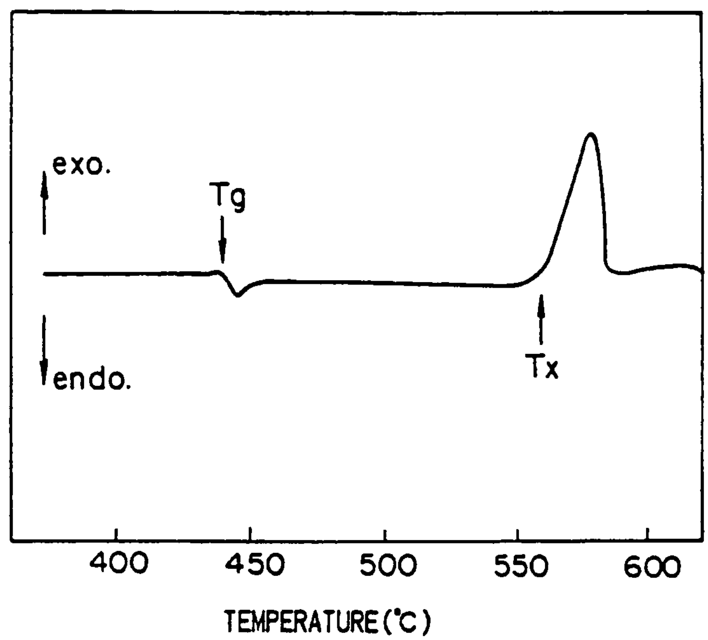

exo.
Tg
endo.
Tx
400
450
500
550
600
TEMPERATURE(°C)

FIG.12

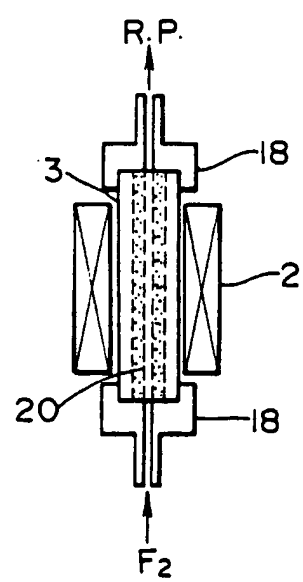

R.P.
18
3
2
20
18
F2

FIG.13

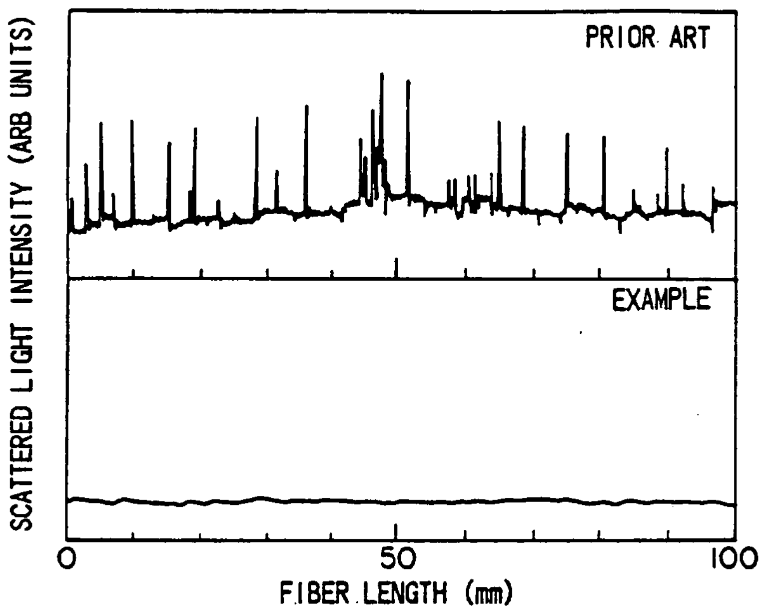
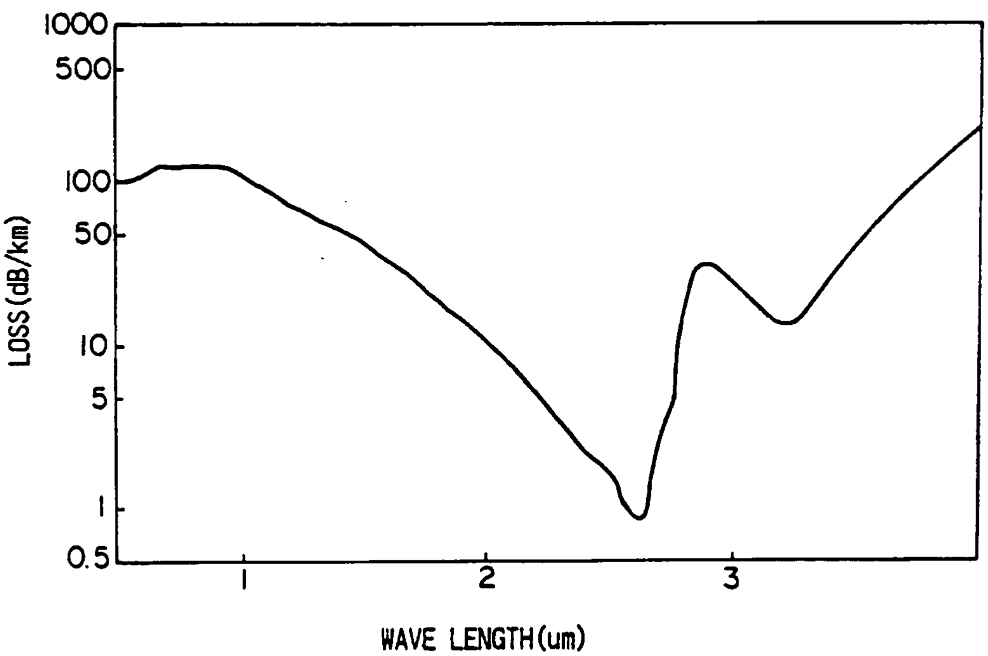

PRIOR ART
EXAMPLE
SCATTERED LIGHT INTENSITY (ARB UNITS)
0
50
100
FIBER LENGTH (mm)

FIG.14


1000
500
100
50
10
5
1
0.5
LOSS (dB/km)
1
2
3
WAVE LENGTH (um)